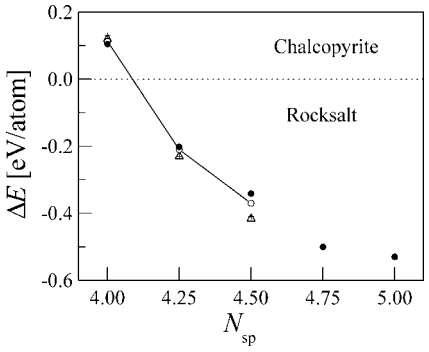

Figure 3. Plot of energy difference per single atom ΔE for different average number of valence electrons N_{sp}. Open triangles (△) represent Au(In,Sn,Sb)Te_2; open circles (○) represent Ag(In,Sn,Sb)Te_2; crosses (+) represent Cu(In,Sn,Sb)Te_2; and solid circles (●) represent AuGaTe2, AuGeTe2, AuAsTe2, InSnTe2, and InSbTe2, respectively. Solid line is the link for Ag series of alloys.

rial has been developed based upon density-functional simulations rather than trial-and-error preparation procedures. In addition, we also expect that materials with N_{sp} above 4.25 will also be good PC materials. This is in excellent agreement with the data compiled in Table 1. In this table we have collected all known phase-change alloys that show good properties in rewritable optical data storage ('successful samples') and also two samples that are not suitable. Consistent with the arguments presented above we note from Table 1 that the N_{sp} of successful PC materials is always larger than 4, and usually between 4.3 and 5. From Figure 3, we estimate that the critical value of N_{sp} that distinguishes the rocksalt and the chalcopyrite structures is about 4.1.

In summary, the DFT calculations presented here help to identify new and possibly superior phase-change materials. All phase-change materials reported are characterized by a cubic or near-cubic coordination, which is caused by the dominance of the p-electron bonding. The average number of valence electrons plays the crucial role in determining the structure of the semiconductor alloys studied here. For $N_{sp} = 4$, we find that the stable structure of (Cu,Ag,Au)$InTe_2$ is the chalcopyrite phase with sp^3-bonding, while for $N_{sp} = 4.5$, the stable structure of (Cu,Ag,Au)$SbTe_2$ ternary alloys is the rocksalt structure with p-bonding. Results show that Te-based ternary materials will favor the suitable rocksalt structure if their N_{sp} is bigger than 4.1. This simple criterion facilitates the search for new phase-change materials and opens the way to a more fundamental understanding of phase-change materials.

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Molecular "Glass" Blowing: From Carbon Nanotubes to Carbon Nanobulbs**

By *Zhenping Zhu*,* *Dangsheng Su*, *Yi Lu*, *Robert Schlögl*,* *Gisela Weinberg*, and *Zhenyu Liu*

Since their discovery and large-scale synthesis,[1] carbon nanotubes (CNTs) have attracted enormous interest due to their various unique physical and chemical properties.[2–4] They exhibit excellent structural flexibility and fluidity and can be bent, collapsed, or deformed into various shapes such as buckles, rings, ribbons, or fullerene onions.[5,6] Here we report a novel behavior of multi-walled carbon nanotubes: they can be blown into large carbon bulbs, just as glass tubes can be blown into spherical devices and vessels such as bulbs and flasks.

CNTs have one-dimensional hollow structures and are capped by hemispherical fullerene domes.[4] The structural similarity between CNTs and fullerenes allows shape transformations from one into the other. It has been shown that CNTs can be deformed into small fullerenes such as C_{60}[7] or large multi-walled fullerene onions[6] through a fragmentation–re-

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construction process. Unlike normal glass blowing, however, blowing CNTs into nanobulbs occurs on a molecular scale and thus is a more difficult process: gases must fill the closed tubes and a pressure difference between the inside and outside of tubes must be provided. All these requirements can be met by a fast exothermal decomposition of explosives as a synthesis strategy. This approach has previously been used to produce diamond and GaN nanoparticles.[8] Graphite nanotubes or onion-like nanostructures have also been observed frequently in the products obtained from the explosive decomposition of various specially synthesized organic or organometallic molecules.[9] We recently reported[10] that multi-walled CNTs can be efficiently obtained by explosive decomposition of picric acid or *m*-dinitrobenzene (two examples of normal commercial explosives) in the presence of a cobalt or nickel catalyst.

In the present case of blowing CNTs into carbon nanobulbs, a mixture of picric acid and nickel formate is employed. The explosive decomposition of the mixture, occurring on a microsecond timescale, generates temperatures of up to 1200 K and a pressure jump of up to 40 MPa. In addition, large amounts of gases (CO, CO_2, N_2, and H_2O) are produced, as well as carbon and nickel species. After the decomposition, the system temperature gradually drops since no heating is provided. The small carbon species assemble into tubular nanostructures, helped by nickel nanoparticles.[10] At the tube growing stage (with opening tube ends[11]), the hot, high-pressure gases are packed inside the tubes to meet a balance between the pressures inside (P_{in}) and outside (P_{out}) the tubules. This balance prevails until the tubes are closed, corresponding to growth termination.[11] Subsequently, the temperature outside the tubes, T_{out}, continues to drop after tube closure due to thermal conductance through the reactor wall and becomes lower than the temperature inside the tubes (T_{in}) because the *c*-axis thermal conductivity of the layered graphitic sheets is intrinsically very low.[12] The difference between T_{in} and T_{out} causes a positive difference between P_{in} and P_{out} and then induces an expansion of the tube volume through structural deformations. This process is similar to normal glass blowing and results in large spherical carbon nanobulbs.

As shown in Figure 1a, the products from the decomposition of the picric acid and nickel formate mixture contain large amounts (about 30 %) of spherical bulbs along with multi-walled carbon nanotubes. Figure 1b shows transmission electron microscopy (TEM) images of two typical bulbs. Most bulbs are partially filled with small nickel particles, as revealed by TEM and energy-dispersive X-ray analyses, although some bulbs with completely empty cores are also evident. Unlike the previously reported onion-like carbon nanoparticles,[9a,c,13] which are normally of the order of several to tens of nanometers in diameter and exhibit relatively narrow internal cages, the bulbs obtained here have diameters of 150–920 nm, peaking at about 320 nm, and exhibit wall thicknesses of 6–25 nm, peaking at 12 nm. The high ratio of diameter to wall thickness (up to 100:1) leaves behind very wide internal cages.

The bulb walls are uniform in thickness over the entire sphere and consist only of carbon, as revealed by electron energy loss spectroscopy (EELS). The C K-edge EELS spectra of the bulb walls obtained at different electron beam orientations (Fig. 2a) reflect the anisotropic electronic properties of

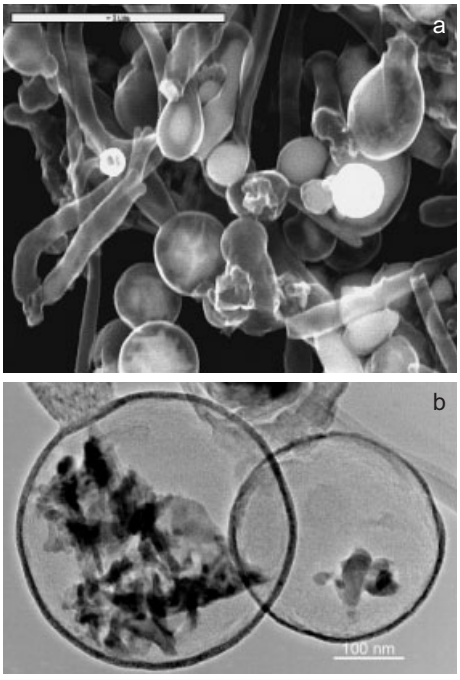

Figure 1. a) SEM image showing that the product contains large spherical bulbs along with carbon nanotubes. Scale bar: ~1 μm b) TEM image of two typical bulbs. The left one is 410 nm in diameter with a wall thickness of 9 nm; the right one is 300 nm in diameter with a wall thickness of 7 nm. The small black objects inside the bulbs are nickel particles.

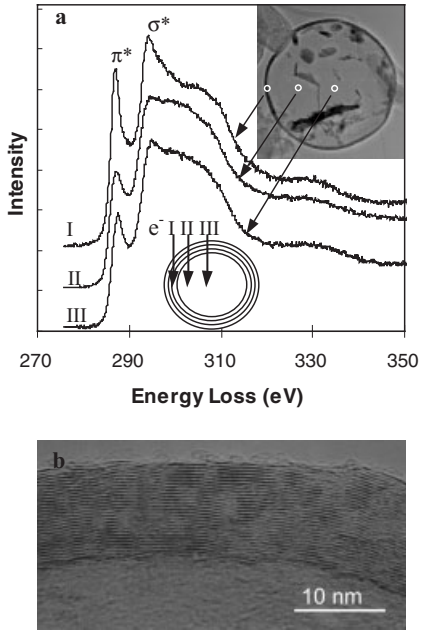

Figure 2. a) C K-edge EELS spectra of a typical spherical bulb obtained when the electron beam is parallel (I), inclined (II), or perpendicular (III) to the graphite (002) planes. b) High-resolution TEM image of the wall of one typical bulb. The interlayer distance is 0.34 nm.

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the bulb walls, which are similar to those of graphite. The π^* contribution is high when the electron beam is nearly parallel to the (002) planes (I) and is reduced, along with a relative increase of the σ^* contribution, when the electron beam is inclined (II) or perpendicular (III) to the planes.[14] High-resolution TEM images (Fig. 2b) further confirm that the walls are constructed of an assembly of concentric graphene shells with "hinge" defects, characteristic also of pre-graphitic sp^2 carbon materials.

Most of the produced bulbs are freestanding and are separated from the carbon nanotubes, but some of them connect chemically with the carbon nanotubes, resulting in bulb–tube assemblies (Fig. 3). These assemblies can be viewed as intermediate derivatives and reflect "frozen" stages during the bulb formation, confirming that the bulbs are formed by tube blowing. For the bulb–tube assemblies, the bulbs are normally located at the ends of the tubes and form flask-like structures (Fig. 3a–c). In this case, the assemblies are always symmetrical in their morphology along the tube axis. Assemblies with bulbs at the middle of bamboo-like tubes, as shown in Figure 3d, are also frequently observed with strong contacts between the bulbs and the tubes. In some assemblies, both the bulbs and the tubes are open with respect to each other (see the left bulb in Fig. 3b). These observations indicate that the bulb–tube assemblies do not result from sample overlapping or from a subsequent random interaction between the bulbs and the tubes after their formation, and suggest that the bulbs grow from the tubes. Furthermore, for all of the bulb–tube assemblies, the bulbs are rather larger in diameter than the tubes, although their walls are much thinner than the tube walls (Fig. 3b–d). These samples are quite distinct from the previously reported flask-like nanostructures[15] formed by depositing carbon species on the outer surfaces of metal particles, in which the wall thickness of the sphere part is higher than that of the tube part and the metal particles are filled completely. The main features of the present bulb–tube assemblies are much more similar to the situation in conventional glass blowing and correspond to a significantly increased volume of the internal cavity relative to the initial situation of the tubes.

The observation of bulb–tube type intermediate derivatives also indicates that the carbon tubes can blow either at tube ends (Fig. 3a–c) or in the middle of bamboo-like tubes (Fig. 3d). This implies that the tube blowing and the related structural deformation are associated with the defects[4,16] in the graphene and with the strains generated from the high bending of the sp^2 bonds in the curved structures, because these defects and strains are concentrated at the tube ends[17] or at the junction of the two compartments in bamboo-like tubes. It has long been known that such defects and strains can induce drastic changes in the physical properties of carbon nanotubes.[5e,16,18,19] Theoretical calculations have shown that in the presence of paired pentagon–heptagon defects, carbon nanotubes could exhibit excellent plastic deformation, without fracture, at low strains and high temperatures.[19] Therefore, we speculate that the defects facilitate the structural deformations following the pressure driven tube blowing and volume expansion. This suggestion is also supported by the observation that most of the nanotubes obtained under the present conditions are not well crystallized, especially the bulb–tube assemblies. As the blowing induced structural deformation causes a large reduction in the number of graphene layers, corresponding to a decreased wall thickness, we propose that the defects derived from an sp^2–sp^3 rehybridization and/or an incomplete bonding (e.g., vacancies and dislocations)[16] make a greater contribution to the blowing.

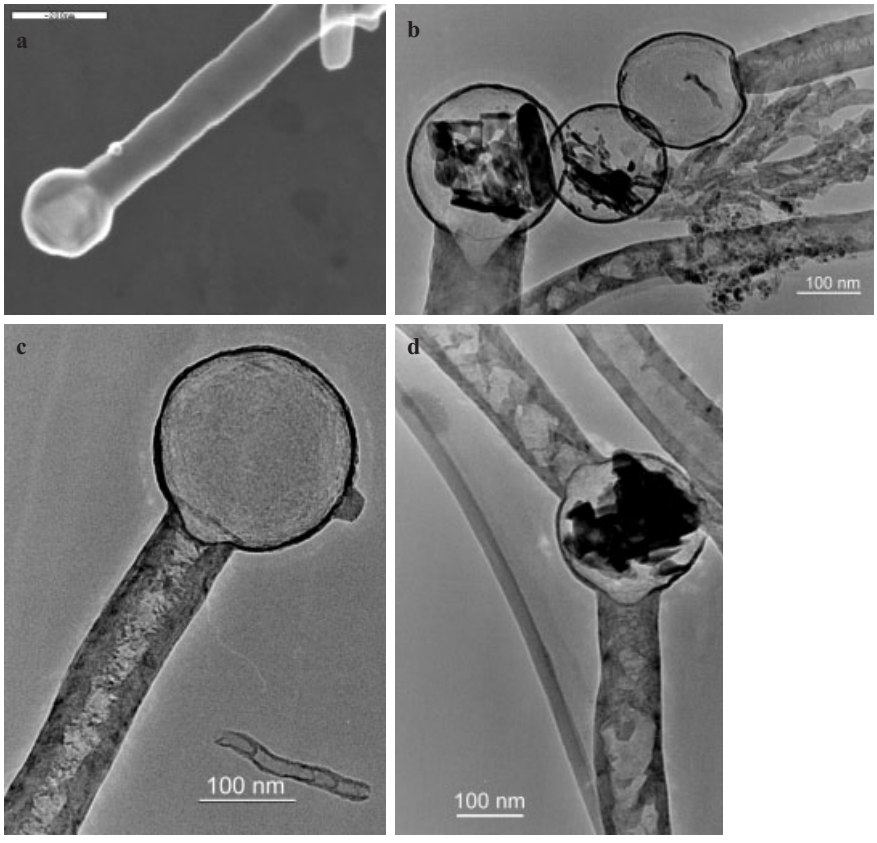

Figure 3. Some intermediate derivatives show that the bulbs are formed from tube blowing. Note the drastic changes in diameter and in wall thickness. a) SEM and b, c) TEM images of bulb–tube assemblies generated from the blowing at tube ends. In the assembly in (c), the wall thickness is 25 nm for the parent tube and 9 nm for the blown bulb. d) One bulb–tube assembly generated from blowing at the middle of bamboo-like tubes. These images also show the gradual deformation procedure (closing up) during the formation of the spherical hollow bulbs.

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Another interesting question is how the freestanding bulbs become detached from the parent tubes. A possible mechanism can be deduced from the special structures of the different intermediate derivatives. At the stage of a bulb being just blown and still communicating with its parent tube through an opening (see the left bulb in Fig. 3b), there should be many dangling bonds at the bulb–tube junctions due to the great change in the number of graphene layers. This open structure is thermodynamically unstable and has a tendency to reach a low energy level by eliminating the dangling bonds and closing up.[4,6a] Figures 3c,d show the situation of the bulb closures. The right bulb–tube assembly in Figure 3b shows a structure with complete closure for both the bulb and the parent tube. In such an assembly, theoretically, the number of pentagon- and heptagon-defects is higher at the bulb–tube junctions as the curling direction of the bulb is different to that of the tube.[16b,20] Further tailoring of the defects leads to a bulb–tube separation.

It should be noted that nickel particles seem not to contribute to the formation of the bulbs from the tubes, despite the fact that they play a key role in the nucleation and growth of the tubes and are frequently filled in the obtained bulbs. This proposal is based on the observation that many bulbs are sparsely filled with metal particles (see the right-hand bulbs in Figs. 1b,3b), and some are even free of them (Fig. 3c). The filled particles (normally dispersed) are probably formed from the tube channels during the blowing. Indeed, metal particles are frequently observed in the channels of some tubes. Unlike the previously reported bamboo-shaped tubes, in which different parts of the nanotube are partitioned by closed thick domes,[21] most of the present tubes, especially the tube moieties in the bulb–tube assemblies (Fig. 3b–3d), only contain very thin carbon ribbons in the tube channels, which probably do not block the channels and allow the decomposition-derived gases to flow freely into the blown bulbs.

As analyzed by selected-area electron diffraction and X-ray diffraction, the nickel particles exhibit the face-centered cubic (fcc) or hexagonal close packing (hcp) single-crystal structure of metallic nickel. As nickel is highly reactive towards inorganic acids, we successfully removed the particles from the bulbs by treatment with 6 M HCl. Figure 4 presents typical bulbs after the treatment, which clearly shows that the bulbs have been completely emptied.

In summary, blowing multi-wall carbon tubes into large carbon nanobulbs is realized in a unique tube growth environment generated by an explosive decomposition of picric acid. The joint action of the filled high-pressure gases and the structural defects in the tubes is responsible for the blowing. The blowing behavior of carbon nanotubes indicates that CNTs exhibit, at least during their generation, excellent thermoplasticity and expansibility, despite the fact that the thermal-expansion coefficient of grown CNTs is near zero.[3] This finding also suggests that it is possible to engineer tubular structures into various shaped devices on a nanoscale by adjusting and controlling the reaction environment. The blown spherical bulbs, characterized by large dimensions, thin walls, and fully hollow cores, are expected to exhibit new physical and chemistry properties and to find some special applications in microcontainers, microreactors, and other devices.

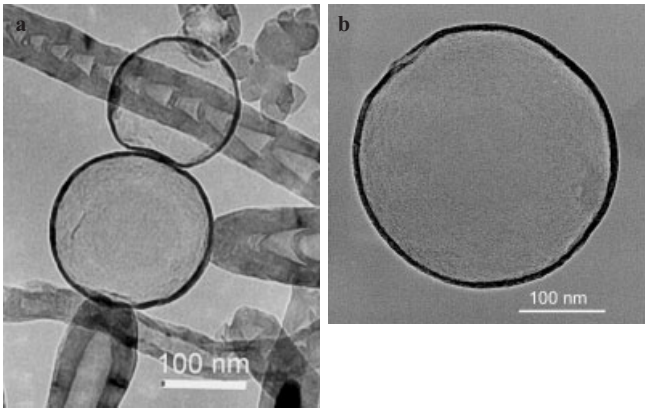

Figure 4. TEM images of the bulbs after a treatment with 6 M HCl. The nickel particles initially contained in the bulbs have been removed, leaving behind completely empty cavities.

Experimental

Picric acid and nickel formate (weight ratio of 3:1–5:1) were mixed physically and loaded into a sealed stainless steel pressure vessel (10.8 mL) with a loading density of 0.25 g mL^{-1}. The decomposition reaction was induced by heating to 583 K at a rate of 20 °C min^{-1}. The reaction, which lasts for only a few microseconds, generated a pressure of about 40 MPa (shock wave, behind which the equilibrium pressure is about 15 MPa) and temperature of about 1200 K. After the reaction, the vessel was cooled to room temperature in air and emptied of gaseous products (predominantly CO, CO_2, N_2, and H_2O, as revealed by gas chromatography), and the solid products were collected. For the acid treatment, 50 mg of sample was added to 100 mL of a 6 M aqueous HCl solution and refluxed for 16 h with magnetic stirring. After the refluxing, the suspension was filtered, washed with deionized water and ethanol, and dried at 110 °C overnight.

SEM images were taken using a Hitachi S-4000 scanning electron microscope with a field-emission gun operating at an accelerating voltage of 15 kV, equipped with an EDAX DX4 energy-dispersive X-ray (EDX) detector. TEM images and electron diffraction patterns were taken using a Phillips CM200 FEG microscope operating at 200 kV. This machine was equipped with a GATAN imaging filter GIF100 for EELS measurement. The samples were prepared by placing one drop of the alcohol suspension on a silicon substrate for SEM analyses or on a carbon-film-supported copper grid for TEM analyses.

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Controlling the Morphology of Multiwalled Carbon Nanotubes by Sequential Catalytic Growth Induced by Phosphorus**

By *Vincent Jourdain*,* *Odile Stéphan*, *Marie Castignolles*, *Annick Loiseau*, and *Patrick Bernier*

Because of their exceptional electric, mechanical, and structural properties, carbon nanotubes are promising materials for a wide range of applications, such as electron field emitters,[1,2] composite additives,[3,4] electronic nanodevices,[5–7] and nanomachine components.[8,9] In view of these application potentials, intensive research has been conducted into control of the parameters crucial for modification of their desired properties. Areas of research include the morphology of the nanotubes,[10–14] insertion of metals or alloys during the synthesis,[15,16] and their positioning.[17,18] Concerning the morphology, it is generally assumed that, in catalytic decomposition, the nanotube's outer diameter correlates with the size of the catalyst particle that generates the tube,[12] while the inner diameter is mainly related to the chemical potential of the carbon atoms dissolved in the catalyst particle.[19,20] Bamboo morphologies, characterized by the periodic inclusion of graphitic layers,[13] are commonly observed, and the frequency of the inclusions appears to correlate with the diameter of the catalyst particle.[21] Coiled or helicoidal morphologies are also frequently synthesized (at temperatures of 500–800 °C) by adding small amounts of sulfur or phosphorus to the transition-metal catalyst.[22–24] At higher temperatures, sulfur is also known to promote filling of the nanotubes with metals and metal sulfides.[16]

Although substantial advances have been made,[14,16,20,25] an enhanced comprehension of the growth mechanism is still needed to design carbon-nanotube-based nanostructures with specific and controllable features. Here, we show that the use of phosphorus as a co-catalyst enables one to sequentially

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